Ab Initio Prediction of ^{15}N-NMR Chemical Shift in α-Boron Nitride Based on an Analysis of Connectivities

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ABSTRACT: Hydrogen-saturated cut-outs of hexagonal boron nitride have been used to model the solid state. Model compounds have been geometry optimized by means of density functional theory, whereas chemical shift calculations have been carried out at the coupled-perturbed Hartree–Fock level of theory employing gauge-including atomic orbital (GIAO) basis sets. The reliability of results has been tested against experimental values for chemical shifts in stable molecules with similar structural elements. With increasing cluster size, viz. a vanishing influence of the saturating hydrogens on the innermost nitrogen atoms, we find a convergence of ^{15}N chemical shifts. A classification scheme for the chemical environment of a nitrogen atom has been set up according to its bonding graph including the second coordination sphere. For a given connectivity, chemical shifts vary within a few parts per million, thus enabling us to predict a ^{15}N-NMR chemical shift of -285 ± 5 ppm for solid α-boron nitride. © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 716–725, 1998

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Introduction

This work has been motivated by the need for structural information on amorphous borosilazane ceramics, which have recently been synthesized from molecular precursors.[1] Early nuclear magnetic resonance (NMR) studies revealed that boron is threefold coordinated to nitrogen in $Si_3B_3N_7$, whereas silicon is tetrahedrally surrounded by nitrogen.[2] For the trivalent nitrogen, four different first neighborhoods are postulated, NB_3, NB_2Si, $NBSi_2$, and NSi_3, which may occur simultaneously. Their ratios of abundance in the amorphous material are still unknown. Measuring the magnetic resonances of its nitrogen nuclei may help getting this information, provided that the chemical shifts of nitrogen atoms in the aforementioned four different chemical environments are known. With this study, we make a first step toward achieving theoretically determined nitrogen NMR data of the ternary system Si/B/N—by investigating the binary compound α-boron nitride.

Boron nitride itself plays a prominent role as a working material. Its layer structure and high temperature resistance are the outstanding features for its usefulness as a high-temperature lubricant, as a heat shield in rocket burners, and so forth. At first glance, it may be surprising that, to the best of our knowledge, up to now no publication has reported on an experimental value for the ^{15}N-NMR chemical shift of this material. There are, however, some technical problems to overcome; for instance, the long spin–lattice relaxation time (T_1) for the low-γ ^{15}N nucleus. A possible clue to the problem is by use of polarization transfer techniques from ^{11}B to ^{15}N, which appear applicable in solid boron nitride.[3] Cross-polarization experiments from ^{27}Al to ^{29}Si (i.e., another transfer from a quadrupole nucleus to an $I = 1/2$ nucleus) were recently reported to be successful, but difficult to conduct.[4]

Quantum chemical calculations of NMR data, on the other hand, have become an increasingly important and reliable tool for structural analysis.[5–12]

Although widespread in molecular computational chemistry, there is no computer code available, to our knowledge, which determines NMR chemical shifts for crystalline materials at the *ab initio* level with periodic boundary conditions. In light of the aforementioned data, we have undertaken a theoretical investigation of the ^{15}N-NMR chemical shift in threefold coordinated B/N molecular clusters and have systematically enlarged the model compounds to reach convergence.

General Procedure

A reliable prognosis for the solid state was achieved in three steps: (1) check of methodological consistency by comparison with experiments; (2) choosing frameworks, optimizing geometries, and calculating chemical shifts of apt clusters; and (3) classification of chemical shifts according to bonding schemes.

To assure consistency within our methodology, and to lend confidence to the chemical shifts obtained, we compared our results with experimentally determined chemical shifts of benchmark compounds with bond characteristics as similar to hexagonal boron nitride as possible.

Test calculations on the smallest binary compounds exhibiting a threefold coordination $B(NH_2)_3$ and $N(BH_2)_3$ have revealed theoretical chemical shifts of -353 and -171 ppm, respectively. Borazine[13] as well as the aforementioned borosilazane ceramics show nuclear magnetic resonances in the region of -260 to -330 ppm.[2] We therefore consider these model compounds too small and thus unsuitable for our purposes. As model clusters, we chose frameworks consisting of planar, six-membered rings—identical to the α-boron nitride structure. Dangling bonds were saturated with hydrogen, resulting in a threefold coordination of both boron and nitrogen. After geometry optimization we determined chemical shifts and classified the obtained values according to the hydrogen content in the first and second coordination spheres with respect to the nucleus in focus.

In addition to monolayer structures, we have performed calculations on a three-layer system aiming to evaluate possible influences of packing on the chemical shift of nitrogen. For these structures, we have optimized the layers separately and assumed an interlayer distance of 3.33 Å, which occurs in α-boron nitride.[14] The long interlayer distance led to the decision to localize additional basis functions in between the layers at half their mutual distances (i.e., 1.1665 Å above and below boron and nitrogen atoms of the mid-element) to check for basis set deficiencies.

Computational Details

GEOMETRY OPTIMIZATIONS

Geometry optimizations have been performed using the DGauss Code[15,16] interfaced to the UniChem suite of programs[17] and the Gaussian-94 program modules.[18] Local density functional (LDF) geometry optimizations were carried out employing the Slater (Dirac) exchange- and Vosko–Wilk–Nusair correlation (S-VWN) functionals. For our purposes, the local density approximation (LDA) has proven to lead to reliable geometries,[19] with the exception of hydrogen bond lengths, which come out slightly too long. Moreover, the reliability of obtained structural properties is demonstrated by the results of our chemical shift calculations reported further in what follows.

All atoms except hydrogen were described by a split valence basis set of double-zeta plus polarization quality (DZP) taken from the Gaussian-94 basis set library. For hydrogen, we dispensed with polarization functions.

To exclude a determination of saddle-point geometries, we calculated the second derivative of the total energy with respect to nuclear coordinates for open-chain systems after having reached stationary points on their potential energy surface (PES).

SINGLE-POINT MAGNETIC AND ELECTRONIC PROPERTIES

Chemical shielding tensors have been calculated at the coupled perturbed Hartree–Fock (CPHF) level making use of the Turbomole program package.[5,20,21] To minimize the effects of gauge dependence, we employed gauge including atomic orbitals (GIAOs)[22] and basis sets of triple-zeta quality with *d*-functions (TZP, 6-311G*) for boron, nitrogen, silicon, and carbon atoms, respectively. Hydrogen was described at a triple-zeta level (6-311G). As above, exponents and coefficients have been taken from the Gaussian-94 basis set library.

Calculated shielding constants are converted to chemical shifts by employing the equation, $\delta_{\text{subst, th}} = \delta_{\text{ref, exp}} + \sigma_{\text{ref, th}} - \sigma_{\text{subst, th}}$, in which the indices denote a theoretical (th) or experimental (exp) determination, the substance of interest (subst), and a reference substance (ref). The experimental reference to which our calculated chemical shift of −237 ppm for the NH_4^+ cation has been adjusted is a saturated aqueous solution of ammonium chloride $NH_4^+Cl^-$ (exp.: −353 ppm).[23] All given values refer to nitromethane $H_3C^{14}NO_2$ as standard.[23] Where other standards have been used in the literature, corresponding values have been shifted by the difference relating nitromethane to the standard employed. Footnotes indicate these cases.

Mulliken population analyses were performed from Roothaan SCF molecular orbitals using Turbomole.

Results and Discussion

VERIFICATION OF METHODOLOGICAL CONSISTENCY

The number of boron- and nitrogen-containing compounds that exhibit structural relations to α-boron nitride and whose chemical shifts have been investigated experimentally is rather small.[13,23–26] On the theoretical side, a considerable amount of work on nitrogen chemical shifts has been accomplished by the Bochum group; however, their works[27–30] and others[31–33] on this topic refer mostly to smaller molecules and/or compounds related to (bio-) organic chemistry.

Figure 1 displays structures of compounds for which experimental values are available and that served us as probe molecules to check for the consistency of our method. Theoretical as well as experimental results may be taken from Table I.

Our calculated chemical shifts agree well to excellently with the observed values—particularly if experimental uncertainties due to the well-known difficulties of measuring ^{14}N shifts with high numerical significance[23] are taken into account. The results reflect the comparatively low importance of electron correlation for the theoretical determination of chemical shifts in this class of compounds on the one hand and the sufficiency of the employed basis set on the other.

CLUSTER CALCULATIONS

Structure formulas of the 11 single-layer model clusters and equilibrium bond lengths obtained are displayed in Figure 2. All clusters are found to be planar. The theoretical B—N bond lengths in the inner cluster regions (i.e., for B—N bonds not directly connected to one of the saturating H atoms) agree with the observed value of boron nitride of 1.446 Å[14] to within ±0.01 Å. Also, the experimentally known bond distance of borazine,

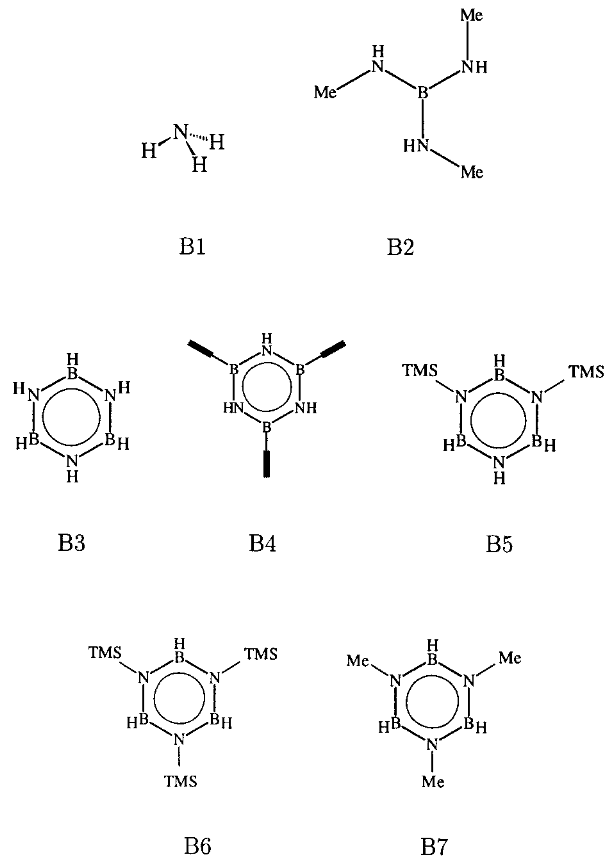


FIGURE 1. Calculated benchmark Compounds, TMS = trimethylsilyl residue—$Si(CH_3)_3$; Me = methyl.

1.429 Å,[34] is well reproduced in the calculations. Nitrogen NMR chemical shifts for compounds **1–11**, determined at their equilibrium geometries, are listed in Table II. The reliability of our chemical shift calculation has already been assessed. We find NMR chemical shifts for ^{15}N-nuclei between −251 and −305 ppm.

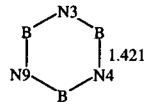
Commonly performed investigations aiming at establishing correlations between chemical shifts (or their constituents) with molecular or atomic properties, such as charges, HOMO/LUMO gap energies, 1*s* orbital energies, etc., generally fail for our molecules. We do find a roughly linear relationship between the trace of the diamagnetic part of the chemical shielding tensor and the total atomic charge; however, because the diamagnetic shift is strongly overcompensated by paramagnetic contributions, total chemical shifts do not correlate with atomic charges. Noteworthy features become visible when relating nitrogen π-atomic populations and total chemical shifts—an idea originally brought up by Spiesecke and Schneider.[35] Our results are displayed in Figure 3.

A coarse data distinction reveals two types of signals: the unique feature of the resonances marked with diamonds is a direct N—H bond, whereas boxes correspond to nitrogen atoms free of hydrogen in the first coordination sphere. Within each block, we find an almost linear correlation of π populations and total chemical shifts. The π populations for hydrogen-bonded nitrogen atoms range from approximately $1.63e_o$ to $1.69e_o$, and hydrogen-free nitrogen atom exhibit π populations between $1.54e_o$ and $1.58e_o$. Among the hydrogen-free nitrogen atoms, minor deviations from a linear correlation occur for compounds **4**, **6**, **8**, and **9** with N:B ratios not equal to one—the consequence of which are unbalanced charges and alternations of the chemical shift, that is, the higher the nitrogen content the more a signal is shifted toward low field values and vice versa.

TABLE I.
^{15}N and ^{14}N-NMR Chemical Shifts (ppm) for Employed Benchmark Molecules—Calculations Based on CPHF Procedure Employing GIAO Basis Sets of TZP Quality (Nitromethane As Standard).

		Nitrogen chemical shifts (ppm)	
Compound[a]	Sum formula	Theoretical	Observed
B1	NH_3	−382	−380[23]
B2	$B(NH(Me))_3$	−349	−352[13]
B3	$(BHNH)_3$	−269	−266(^{14}N[b])[24]
B4	$(BC_2HNH)_3$	−269	−269[26c]
B5	$B_3H_3N_3(TMS)_2H$	−264 (N — H), −265	−255 (^{14}N — H), −261 (^{14}N)[24]
B6	$(BHN(TMS))_3$	−252	−256 (^{14}N)[24]
B7	$(BHN(Me))_3$	−273	−267 (^{14}N)[24]

[a] See also Figure 1.
[b] ^{14}N and ^{15}N chemical shifts are identical within error bars of their measurement.[38]
[c] The value of −266 ppm, given by Bonhomme et al.,[26] refers to $NH_4(^{15}NO_3)$ as standard.



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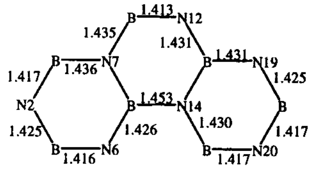

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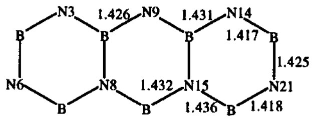

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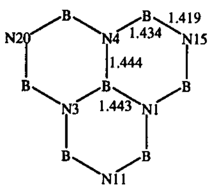

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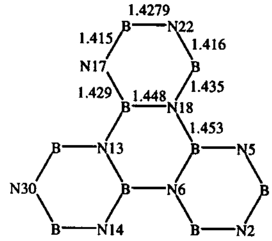

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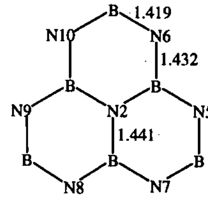

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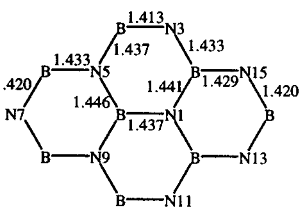

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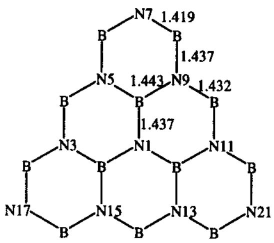

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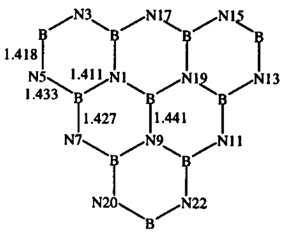

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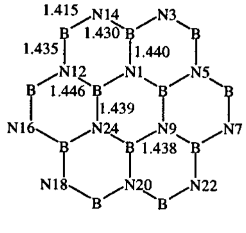

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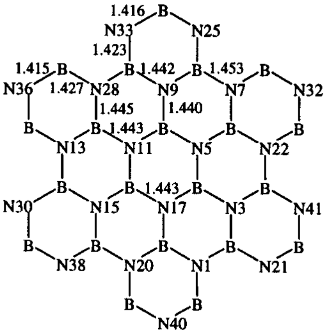

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FIGURE 2. *Ab initio* equilibrium geometries obtained for boron nitride cut-outs. Geometries were determined by LDA-DFT optimizations employing DZP basis sets (bond lengths given in angstroms). For reasons of clarity, π-electrons and hydrogens saturating the dangling bonds of the outer B and N atoms have been omitted.

TABLE II.
Nitrogen Chemical Shifts of Single-Layer Compounds — Values Obtained at CPHF Level Employing GIAOs and TZP Basis Sets (Refer to Fig. 2 for Assignments).

Compound	Sum formula	Nitrogen atoms	Chemical shift (ppm)	Class
1	$B_3N_3H_6$	3, 4, 9	−269	●
2	$B_7N_7H_{10}$	2	−269	●
		7	−254	▲
		6	−284	▼
		6	−284	▼
		6	−284	▼
		12	−284	▼
		14	−275	♦
		19	−285	▼
		20	−270	●
3	$B_7N_7H_{10}$	6, 21	−270	●
		3, 14	−287	▼
		8, 15	−252	▲
		9	−304	■
4	$B_7N_6H_9$	1, 3, 4	−253	▲
		11, 15, 20	−264	●
5	$B_9N_9H_{12}$	2, 22, 30	−270	●
		5, 14, 17	−283	▼
		6, 13, 18	−274	♦
6	$B_6N_7H_9$	2	−287	★
		6, 5, 7, 8, 9, 10	−290	▼
7	$B_8N_8H_{10}$	1	−285	★
		7	−265	●
		5, 9	−255	▲
		3, 11	−283	▼
		13, 15	−290	▼
8	$B_{12}N_{10}H_{12}$	7, 17, 21	−264	●
		1	−280	★
		3, 5, 9, 11, 13, 15	−251	▲
9	$B_{10}N_{12}H_{12}$	3, 5, 13, 15, 20, 22	−290	▼
		7, 11, 17	−305	■
		1, 9, 19	−289	★
10	$B_{12}N_{12}H_{12}$	1, 9, 24	−284	★
		5, 12, 20	−257	▲
		3, 7, 14, 16, 18, 22	−284	▼
11	$B_{21}N_{21}H_{18}$	3, 9, 15	−284	★
		5, 11, 17	−285	★
		1, 7, 13, 20, 22, 28	−273	♦
		21, 25, 30, 33, 38, 41	−287	▼
		32, 36, 40	−266	●

An infinite solid state material with equal amounts of N and B is expected to show the same absolute value of atomic charges for nitrogen and boron. Compound **11**, whose nitrogen atoms are least saturated with hydrogen compared with the other clusters, exhibits nearly balanced charges on the innermost atoms of $-0.47e_o$ on N, and $+0.52e_o$ on B, respectively, supporting its sufficiency in size with respect to predictions for the solid state.

A further and finer examination of the data given in Figure 3 shows that one can clearly distinguish three groups of "signals" in each block. To each group a unique chemical environment could be assigned, including neighbors up to the second coordination sphere. Connectivities of the six different environments encountered have been marked by different symbols and are displayed in Figure 4. The classification of the nitrogen atoms in

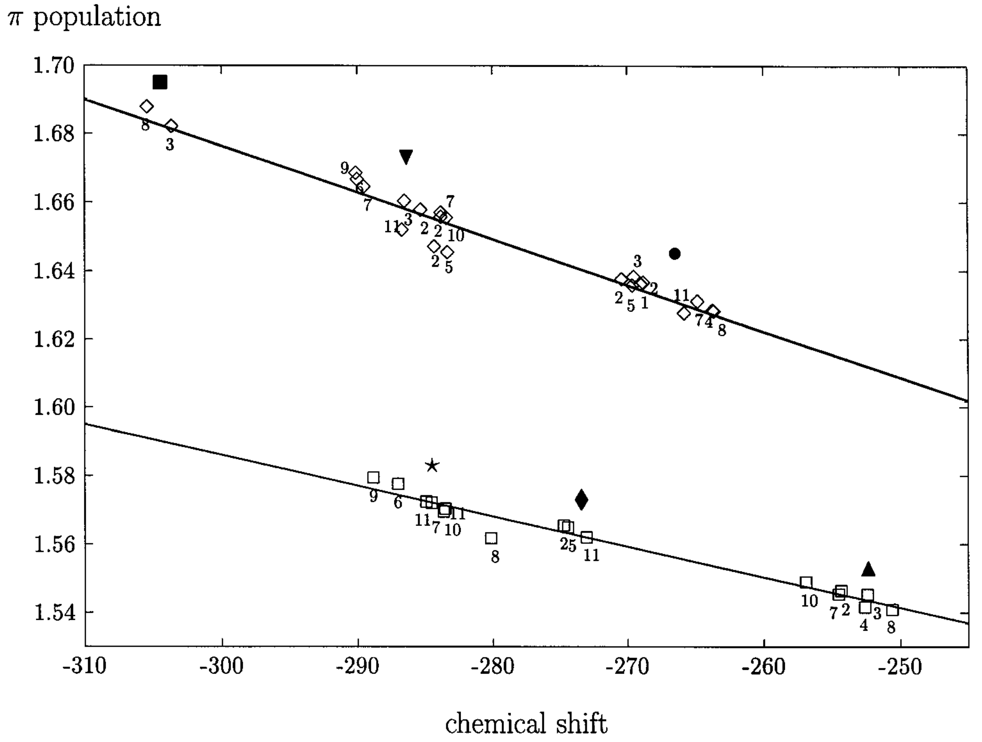

FIGURE 3. Calculated nitrogen chemical shifts for boron nitride cut-outs vs. π-electron population at the specific center. Classification of centers according to scheme presented in Figure 4; numbers refer to compound labels in Figure 5.

our set of single-layer model compounds is visualized with the help of these symbols in Figure 5 and Table II. Table III summarizes our findings, assigning an average chemical shift to each specific chemical environment.

Nitrogen atoms that are surrounded solely by boron and nitrogen up to the second coordination sphere are marked with a star; their bonding situation resembles most closely the one in pure boron nitride layers. Upon comparison of the calculated

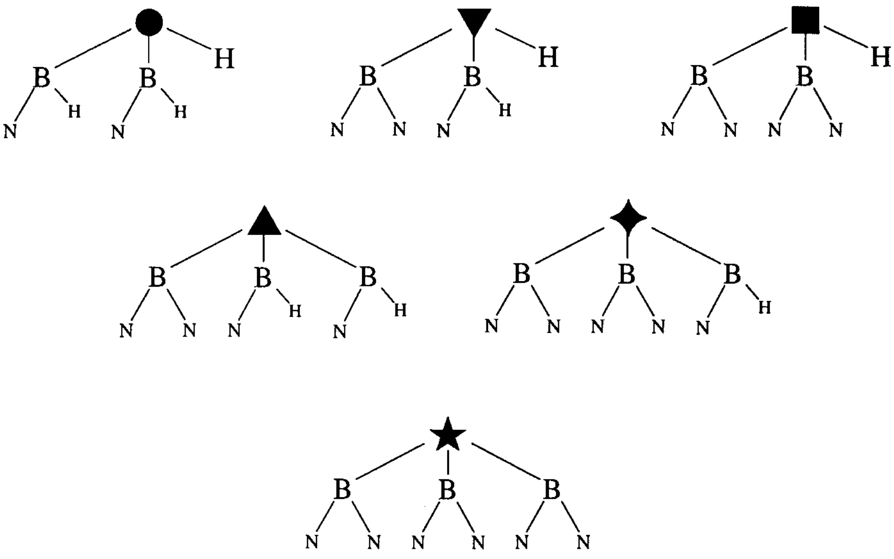

FIGURE 4. Schematic representation of coordination with respect to nitrogen atoms (symbols) in calculated compounds.

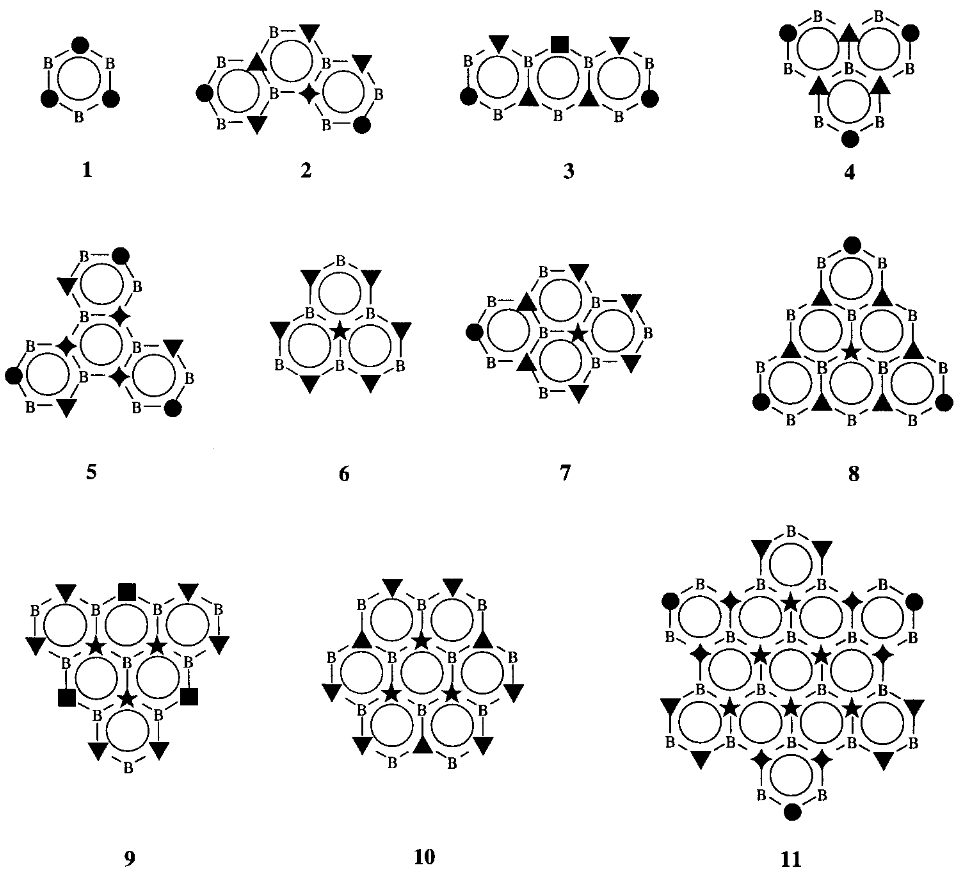

FIGURE 5. Calculated single-layer boron nitride cut-outs. Geometries optimized by LDA-DFT methods employing a DZP split valence basis set; clusters are saturated with hydrogen. Symbols are explained in Figure 4.

chemical shifts of the star labeled nitrogen atoms in the largest compound (**11**), only a slight difference between the innermost three nitrogen atoms and the next shell of nitrogen atoms is observed. In view of this finding, and considering the almost balanced charge distribution in this compound (discussed earlier), and, finally, the narrow distribution of calculated chemical shifts in this chemical environment, we regard a theoretical value of −285 ppm as converged for a two-dimensional infinite layer of boron nitride.

TABLE III.
Average Chemical Shifts for Nitrogen Atoms According Bonding Classes Given (Minimum and Maximum Deviations from Mean Value Shown in Parentheses).

Nitrogen	Chemical shift (ppm)	Occurrence
●	−267 (+1 / − 3)	20
▼	−287 (+4 / − 3)	36
■	−305 (+1 / − 1)	10
▲	−253 (+2 / − 4)	17
♦	−274 (+1 / − 1)	10
★	−285 (+5 / − 4)	15

An infinite, single-layer model compound for hexagonal boron nitride should exhibit an axially symmetric shielding tensor, which means the principal components σ_{11} and σ_{22} of the total shielding tensor perpendicular to the principal axis z should be equal. Thus, with increasing cluster size, a convergence of their difference toward zero is expected and was found in this work. Results obtained are displayed in Table IV. For the largest compound (**11**), the differences amount to 1 ppm for the innermost nitrogen atoms to below 1 ppm. One should keep in mind that, for an atomic center exhibiting D_{3h} symmetry, σ_{11} and σ_{22} are equal, which can be shown by group theoretical considerations.[36]

So far, however, only single-layer models have been considered. An estimate of packing effects on

TABLE IV.
Absolute Values for Difference of In-Plane Components σ_{11} and σ_{22} of Total Chemical Shielding Tensor for Compounds Containing Star-Labeled Nitrogen Atoms (ppm).[a]

Compound	Atom number	$\|\sigma_{11} - \sigma_{22}\|$	Remarks
6	2	0	Zero due to symmetry
7	1	6	
8	1	0	Zero due to symmetry
9	1, 9, 19	5	
10	1, 9, 24	3	
11	3, 9, 15	1	
	5, 11, 17	0	

[a] The *z*-axis is perpendicular to the molecular plane. For compound assignment and atom numbering, refer to Figure 2.

the nitrogen chemical shift can be obtained by extending the model to multilayer systems. As shown by the calculations on the three-layer model (Fig. 6), there are only slight differences when comparing this system with its corresponding "building elements," namely compounds **4** and **6**. The chemical shift of the central nitrogen is increased by merely 4 ppm in the sandwiched layer (cf. Table V). We expect an even smaller packing effect for our largest model compound (**11**).

Because interlayer distances are quite long (3.33 Å), one might suspect that interlayer bonding might not be properly described with basis functions located solely at atomic centers within the layers. We have checked this by putting 13 additional sets of basis functions consisting of one *s* and one *p* orbital each at grid points halfway between two layers, thus enlarging the entire basis set by a total of 104 Cartesian Gaussians. Absolute

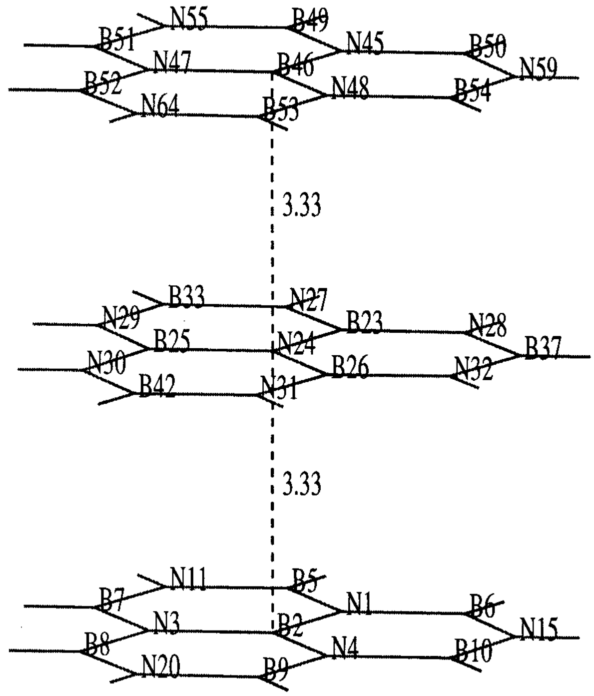

FIGURE 6. Three-layer system of B / N clusters to check for packing effects on the nitrogen chemical shift. Layers have been optimized individually; the interlayer distance has been chosen to be identical to the one observed in α-boron nitride (3.33 Å).

chemical shifts appear to be unaltered upon this particular basis set augmentation and thus this procedure reveals a sufficient basis set within our framework (cf. Table V). This result is further corroborated by a recent study of basis set saturation effects in periodic Hartree–Fock calculations on hexagonal boron nitride that reveals unbound boron nitride layers when calculated at the Hartree–Fock level of theory.[37] In summary, packing effects on the nitrogen chemical shift in layered α-boron nitride should amount to, at most, 5 ppm.

TABLE V.
Results for Chemical Shift Calculations on Three-Layer Systems without and with Additional Functions in between the B / N Layers.[a]

	Chemical shift (ppm)		
Nitrogen atoms	No additional basis functions	additional interlayer basis functions	Class
1, 3, 4, 45, 47, 48	−253 (−253)	−253	▲
11, 15, 20, 55, 59, 64	−264 (−264)	−264	●
24	−283 (−287)	−283	★
27, 28, 29, 30, 31, 32	−285 (−290)	−284	▼

[a] Refer to Figure 6 for numbering. Corresponding single-layer values are shown in parentheses.

Summary

Mono- and three-layer structural elements of α-boron nitride, saturated with hydrogen atoms at the dangling bonds, have been used to obtain a theoretical estimate of the solid-state ^{15}N-NMR chemical shift. We have been able to identify six different chemical environments in our model compounds, differing in their hydrogen content in the first and second coordination spheres. To each of these environments a mean ^{15}N chemical shift has been assigned. The calculated chemical shifts in the monolayer hydrogen-free surrounding have converged with cluster size to a value of about −285 ppm. Judging error bars from a conservative estimate of packing effects due to the multilayer structure, a value of -285 ± 5 ppm for solid-state α-boron nitride ^{15}N nuclei is reasonable.

Acknowledgments

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